氏　　名	Pengoubol Sarntamon（ペングボン サーンタモーン）
学位の種類	博士（理学）
学位記番号	理工博　第 300 号
学位授与の日付	令和元年 9 月 4 日
課程・論文の別	学位規則第 4 条第 2 項該当
学位論文題名	Precise Synthesis of Ultrahigh Molecular Weight Polymers by Polymerization of Long Chain α-Olefins and their Functionalization 遷移金属触媒による長鎖α-オレフィンの重合による超高分子量ポリマーの合成と官能基化（英文）
論文審査委員	主査　教授　野村　琴広 委員　教授　清水　敏夫 委員　准教授　稲垣　昭子 委員　教授　黒川　秀樹（埼玉大学）

【論文の内容の要旨】

Polyolefins (polyethylene, polypropylene) produced by metal catalyzed olefin polymerization are important synthetic polymers in industry, and synthesis of new polymers with specified functions is the attractive research subject.[1] Amorphous poly(α-olefin)s, especially ultrahigh molecular weight poly(α-olefin)s, attract considerable attention in terms of the expecting unique characteristics as cylindrical materials as well as their high melt-flow rate with low density (applied as hot-melt applications etc.). However, examples for the synthesis have been limited so far,[2] because ordinary molecular catalysts exemplified as metallocene afforded low molecular weight oligomers.[2a,3] This is also because that only grafting through approach (polymerization of long chain α-olefin) should be adopted due to all hydrocarbon main/side chains.

In this thesis, synthesis of ultrahigh molecular weight polymers by polymerization of long chain α-olefins (grafting through approach) and their functionalization by an introduction of reactive functionality into the side chain (outside of the cylindrical polymer materials) has been studied. The thesis consists of (i) synthesis of ultrahigh molecular weight long chain α-olefins[3] and (ii) synthesis of ultrahigh molecular weight long chain α-olefins containing reactive functionality by incorporation of functionalized

long chain α-olefins.

Results and Discussion

1. Synthesis of Ultrahigh Molecular Weight Long Chain Poly(α-olefin)s

Polymerizations of 1-octene (OC), 1-decene (DC), 1-dodecene (DD), 1-hexadecene (HD), 1-octadecene (OD) by nonbridged half-titanocene, Cp*$TiCl_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**1**, Cp* = C_5Me_5),[4] linked half-titanocene [$Me_2Si(C_5Me_4)(N^tBu)$]$TiCl_2$ (**2**, known as efficient catalyst for ethylene/α-olefin copolymerization), and ordinary metallocene Cp_2ZrCl_2 (**3**) were studied in the presence of MAO cocatalyst.[3] Catalyst **1** showed the high activities affording high molecular weight polymers with unimodal molecular weight distributions, and the activities by **2** were lower than **1** conducted under the same conditions. In contrast, the reaction by **3** afforded low molecular weight oligomers with the high activities, as reported in the reaction with 1-hexene by *rac*-[Et(indenyl)$_2$]$ZrCl_2$ borate catalyst.[2a] The results thus suggest that **1** should be more suited because the resultant polymers possessed narrow molecular weight distributions (favored propagation compared to chain transfer) and the M_n values were not affected by the Al/Ti molar ratios (suggesting that the probable chain transfer reaction would be β-hydrogen elimination).

On the basis of previous report concerning "quasi" living polymerization of 1-hexene,[5] polymerizations of 1-octene (OC), 1-decene (DC), 1-dodecene (DD), 1-tetradecne (TD) using Cp*$TiMe_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**4**) - [Ph_3C][$B(C_6F_5)_4$] catalyst system in the presence of Al^{i}Bu$_3$ and Al(n-C_8H_{17})$_3$ were explored. The catalyst system showed significant catalytic activities afforded ultrahigh molecular weight polymers with relatively low PDI values [poly(DC), poly(DD): M_n = 2.55-6.74×10^5, M_w/M_n = 1.11-1.68] in all cases under optimized conditions, and linear relationships between the M_n value and the TON (polymer yield) consistent with low PDI values were observed. The ratio of Al^{i}Bu$_3$/Al(n-C_8H_{17})$_3$ affects the activity, and the PDI values became low with the low Al^{i}Bu$_3$ percentage. The PDI values were also affected by the polymerization temperature; the polymers prepared at -40 and -50 °C possessed low PDI values (M_w/M_n = 1.11-1.29).

Linear relationships between the M_n values and the polymer yields (TON), consistent with low PDI values were observed, clearly suggesting that the polymerizations proceeded in a (quasi) living manner. The polymerization behaviors kept even with 1-tetradecene (M_n = 3.06-10.2×10^5, M_w/M_n = 1.19-1.43), and this is the first successful examples for synthesis of ultrahigh molecular weight polymers (polyolefin cylinders) by polymerization of long chain α-olefins (such as DD, TD) and the

controlled synthesis by the living polymerization.

2. Synthesis of Ultrahigh Molecular Weight Long Chain Poly(α-olefin)s Containing Reactive Functionality.

Based on the results in polymerization of DC, DD, and TD in the presence of $Cp^*TiMe_2(O\text{-}2,6\text{-}^iPr_2C_6H_3)$ (**4**) - $[Ph_3C][B(C_6F_5)_4]$ catalyst system, the polymerizations in the presence of non-conjugated dienes (1,9-decadiene, 1,11-decadiene, 1,13-tetradecadiene) were conducted under the similar conditions, on the basis of 1-ocetene/1,7-octadiene polymerization using **1** – MAO catalyst system.[6] It turned out that the copolymerizations of 1-decene with 1,9-decadiene as well as 1-dodecene with 1,11-dodecadiene, 1-tetradecene with 1,13-tetradecadiene proceeded without significant decrease in the activity, affording ultrahigh molecular weight polymers with low PDI values. As observed in the homo polymerizations, good linear relationships between the M_n value and TON were observed in all cases, suggesting a possibility of living polymerization. The resultant polymers are copolymers containing terminal olefinic double bonds as the side chain, confirmed by NMR spectra. Moreover, the copolymerization of 1-decene with 9-decen-1-ol afforded poly(decene-co-9-decen-9-ol) with ultrahigh molecular weights as well as with low PDI values; an incorporation of hydroxy group was confirmed by subsequent chemical modification. Therefore, successful synthesis of long chain poly(α-olefin)s containing reactive functionalities at side chain (outside the cylindrical structure) has been achieved by adopting this polymerization technique.

Conclusion

The results through this thesis demonstrate a precise synthesis of ultrahigh molecular weight polymers (polyolefin cylinder) by polymerization of long chain α-olefins using aryloxo-modified half-titanocene catalyst. The method also enables an introduction of reactive functionalities into the side chain (modification of the cylinder surface). The approach should be highly promising in terms of synthesis of new polyolefin materials by precise polymerization.

References

[1] For example, Nomura, K. *Dalton Trans.* **2009**, 8811.

[2] (a) Saito, J.; Suzuki, Y.; Fujita, T. *Chem. Lett.* **2003**, *32*, 236. (b) Fujita, M.; Seki, Y.; Miyatake, T. *J. Polym. Sci. PartA: Polym. Chem.* **2004**, *42*, 1107. (c) Fries, A.; Mise, T.;

Matsumoto, A.; Ohmori, H.; Wakatsuki, Y. *Chem. Commun.* **1996**, 783.
[3] Nomura, K.; Pengoubol, S.; Apisuk, W. *RSC Adv.* **2016**, *6*, 16203.
[4] (a) Nomura, K.; Komatsu, T.; Imanishi, Y. *J. Mol. Catal. A: Chemical* **2000**, *152*, 249.
(b) Nomura, K.; Komatsu, T.; Imanishi, Y. *J. Mol. Catal. A: Chemical* **2000**, *159*, 127.
[5] Nomura, K.; Fudo, A. *J. Mol. Catal. A: Chemical* **2004**, *209*, 9.
[6] Nomura, K.; Liu, J.; Fujiki, M.; Takemoto, A. *J. Am. Chem. Soc.* **2007**, *129*, 14170.